PESTICIDE SURFACE WATER AND SEDIMENT QUALITY REPORT

DECEMBER 2001 SAMPLING EVENT



Richard J. Pfeuffer
Francine Matson
South Florida Water Management District
3301 Gun Club Road
West Palm Beach, FL 33406

Pesticide Monitoring Project Report December 2001 Sampling Event

Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water and sediment samples from 40 sites were collected from December 16 to December 19, 2001, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, metolachlor, metribuzin, norflurazon, prometryn, and simazine, along with the insecticides/degradates atrazine desethyl, atrazine desisopropyl, diazinon, and endosulfan sulfate were detected in one or more of these surface water samples.

The only diazinon concentrations detected (0.053 μ g/L at S38B), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, these levels are greater than the calculated chronic toxicity (0.04 μ g/L) for *Daphnia magna*. For this compound, at these levels, long term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures.

The herbicides ametryn, bromacil, diuron, and norflurazon, together with the insecticides/degradates DDD, DDE, and DDT, were found in the sediment at several locations, along with one PCB compound. Some of the detected DDD, all of the DDE and one PCB compound sediment concentrations are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. All of the DDT and one of the PCB and DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at these particular sampling sites.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards applies. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-six pesticides and degradation products were analyzed for in samples from all of the 40 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical

quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994a) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC₅₀ or LC₅₀ reported in the summarized literature. Sediment concentrations are compared to coastal sediment quality assessment guidelines (FDEP, 1994b), as there are no corresponding freshwater sediment quality assessment guidelines. A value below the threshold effects level (TEL) should not have an impact on wildlife. The value between the TEL and probable effects level (PEL) has a possibility for impacts, while those exceeding the PEL have a substantial probability for impacting wildlife. This summary covers surface water and sediment samples collected from December 16 to December 19, 2001.

Findings and Recommendations

At least one pesticide was detected in surface water at 27 of the 40 sites and in sediment at 9 of the 36 sites. Sediment samples are not routinely collected at GORDYRD, CR33.5T, NSIDWC06, and NSIDWC07. The concentrations of the pesticides detected at each of the sites are summarized for the surface water and sediment in Tables 2 and 3, respectively. All of these compounds have previously been detected in this monitoring program.

The only diazinon concentrations detected (0.053 μ g/L at S38B), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, these levels are greater than the calculated chronic toxicity (0.04 μ g/L) for *Daphnia magna*. For this compound, at these levels, long term exposure can cause impacts to macroinvertebrate populations, but the pulsed nature of agricultural runoff releases to the canal system precludes drawing any conclusions about the effects of long term average exposures.

Some of the detected DDD, all of the DDE, and one PCB compound sediment concentrations are usually associated with the potential for impacting wildlife when compared to coastal sediment quality assessment guidelines. All of the DDT and one of the PCB and DDD detections were of a magnitude considered to represent significant and immediate hazard to aquatic organisms in coastal sediments. However, there are no corresponding freshwater sediment quality assessment guidelines to further evaluate potential hazards at the District's sampling sites.

The above findings must be considered with the caveat that pesticide concentrations in surface water and sediment may vary significantly in relation to the timing and magnitude of pesticide

application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

 $\underline{2,4-D}$: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The only 2,4-D concentration was detected at ACME1DS (6.4 μ g/L) (Table 2). Using these criteria, these levels should not have an acute impact on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > $10 \,\mu\text{g/L}$ (Verschueren, 1983). Environmental fate and toxicity data in Tables 4 and 5 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.0097 to 0.70 μ g/L. Using these criteria, these surface water levels should not have an acute, detrimental impact on fish or aquatic invertebrates. The sediment concentrations were 8.0 (S2) and 33 (S4) μ g/Kg. However, no sediment quality assessment guidelines have been developed for ametryn.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μ g/L for bluegill and fathead minnow (Verschueren, 1983). The atrazine surface water concentrations found in this sampling event at 21 of the 40 sampling locations, ranged from 0.0098 to 4.9 μ g/L. The highest surface water concentrations of atrazine found in this sampling event (3.7 μ g/L at S4 and 4.9 μ g/L at S2) could inhibit algal cell multiplication. Possible impacts could occur to the base of the food chain. Atrazine was not quantified in the sediment.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to

atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low median DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 6). Most of the sites fall in this category with the exception of S3. The DAR value of 0.3 suggests that some degradation of atrazine has occurred in this basin. However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at S79 (0.86 μ g/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish. Bromacil was not quantified in the sediment.

<u>DDE</u>, <u>DDD</u>, <u>DDT</u>: DDE is an abbreviation of **d**ichloro**d**iphenyldichloro**e**thylene [2,2-bis(4-chlorophenyl)-1,1-dichloroethene]. DDE is an environmental dehydrochlorination product of DDT (**d**ichloro**d**iphenyl**t**richloroethane), a popular insecticide for which the USEPA cancelled all uses in 1973. The large volume of DDT used, the persistence of DDT, DDE and another metabolite, DDD (**d**ichloro**d**iphenyl**d**ichloroethane), and the high K_{oc} of these compounds accounts for the frequent detections in sediments. The large hydrophobicity of these compounds also results in a significant bioaccumulation factor (Table 4). In sufficient quantities, these residues have reproductive effects in wildlife and carcinogenic effects in many mammals.

Sediment quality assessment guidelines have been developed for several metals and organic compounds in coastal sediments (FDEP, 1994b). The DDD concentrations detected range from 1.5 to 13 μ g/Kg. Those values, which are between the TEL (1.2 μ g/Kg) and PEL (7.8 μ g/Kg), have the possibility for impacting wildlife. One value (13 μ g/Kg at S5A) exceeds the PEL and is considered to represent significant and immediate hazard to aquatic organisms.

The TEL is 2.1 μ g/Kg and the PEL is 374 μ g/Kg for DDE in coastal sediments. All of the DDE concentrations detected (8.0 to 40 μ g/Kg) are between the TEL and PEL. The levels between the TEL and PEL have the possibility for impacting wildlife as they have exceeded the threshold level.

The only DDT concentration detected (150 μ g/Kg at S5A) exceeds the PEL (4.8 μ g/Kg). This level is considered to represent a significant and immediate hazard to aquatic organisms.

<u>Diazinon</u>: Diazinon is a non-systemic insecticide and acaricide registered for use on a wide range of crops including citrus, bananas, vegetables, potatoes, sugarcane, rice and ornamentals. Environmental fate and toxicity data in Tables 4 and 5 indicate that diazinon (1) is easily lost from soil by surface solution, with a moderate loss from leaching, and minimum loss from surface adsorption; (2) is slightly toxic to mammals and relatively toxic to fish; and (3) does not bioaccumulate significantly. The only diazinon concentrations detected (0.053 μ g/L at S38B), should not have an acute, detrimental impact on fish. However, for aquatic invertebrates, these levels are slightly greater than the calculated chronic toxicity (0.04 μ g/L) for *Daphnia magna*, a sensitive indicator species for aquatic macroinvertebrates.

Diuron: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96-hour LC₅₀ of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour LC₅₀ of 1.4 mg/L for water fleas and a 96 hour LC₅₀ of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μ g/L (Verschueren, 1983). The highest surface water concentration of diuron found during this sampling event was 0.30 μ g/L (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae. Diuron was detected in the sediment at G123 (49 μ g/K). However, no sediment quality assessment guidelines have been developed for diuron.

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The surface water detection occurred at S178 (0.028 μ g/L). No FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate, nor do these concentrations exceed the Florida Class III surface water standard of 0.056 μ g/L, for the parent compound, endosulfan.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC₅₀ of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at S140 (0.13 μg/L) should not have an acute impact on fish or aquatic invertebrates.

<u>Metolachlor</u>: Metolachlor is a selective herbicide used on potatoes, sugarcane, and some vegetables. Environmental fate and toxicity data in Tables 3 and 4 indicate that metolachlor (1) has a large potential for loss due to leaching and a medium potential for loss in surface solution and due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not

bioconcentrate significantly. Metolachlor is non-toxic to birds (Lyman et al., 1990). The highest surface water concentration found in this sampling event (0.13 μ g/L at S2) is over two orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have a harmful impact on fish or aquatic invertebrates.

Metribuzin: Metribuzin is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, sugarcane, and peas. Environmental fate and toxicity data in Tables 4 and 5 indicate that metribuzin (1) has a large potential for loss due to leaching, a medium potential for loss in surface solution, and a small potential for loss due to surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of metribuzin detected was $0.025~\mu g/L$ (S178). Using these criteria, this surface water level should not have an acute impact on fish or aquatic invertebrates. No metribuzin was detected in the sediment.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 4 and 5 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.035 to 1.3 μ g/L. Even at the highest concentration, this is over an order of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates. Norflurazon was also detected in the sediment at S80 (15 μ g/Kg). However, no sediment quality assessment guidelines have been developed for norflurazon.

PCBs: Polychlorinated biphenyls (PCBs) is the generic term for a group of 209 congeners that contain a varying number of substituted chlorine atoms on one or both of the biphenyl rings. PCB-1254 is a commercial grade mixture containing 54% chlorine by weight. Production of PCBs was banned in 1978 and closed system uses are being phased out. In natural water systems, PCBs are found primarily sorbed to suspended sediments due to the very low solubility in water (Callahan et al., 1979). The tendency of PCBs for adsorption increases with the degree of chlorination and with the organic content of the adsorbent. While the production ban, phase out of uses, and stringent spill clean-up requirements have significantly reduced environmental loadings in recent years, the persistence and tendency to accumulate in sediment and bioaccumulate in fish, make this class of organochlorine compounds especially problematic. Florida sediment quality assessment guidelines have been developed for total PCBs in coastal sediments (FDEP, 1994b). However, an evaluation of the reliability of the sediment quality assessment guidelines for total PCBs suggests a low degree of confidence can be placed on these guidelines due to the insufficient data used in their development. The TEL is 21.6 µg/Kg and the PEL 189 μg/Kg for PCB's. The sediment residue detected at S79 (90 μg/Kg) has a possibility for impacting wildlife, while the concentration detected at S5A (310 µg/Kg) represents a significant and immediate hazard to aquatic organisms. None of the PCB congeners were detected in the surface water

<u>Prometryn</u>: Prometryn is a selective systemic herbicide used on a variety of crops including potatoes, tomatoes, beans, and peas (Hartley and Kidd, 1987). Environmental fate and toxicity data in Tables 3 and 4 indicate that prometryn: (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioaccumulate significantly. The only concentration of prometryn detected was $0.021~\mu g/L$ at structure S6. Using these criteria, this level should not have an acute impact on fish.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 4 and 5 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μ g/L (Verschueren, 1983). Aquatic invertebrate LC₅₀ toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine was detected at S79 (0.40 μ g/L), below any level of concern for fish or aquatic invertebrates. No simazine was detected in the sediment.

Quality Assurance Evaluation

Five duplicate samples were collected at sites S9, S18C, S5A, S3, and S78. All the analytes detected in the surface water had precision $\leq 30\%$ RPD. No analytes were detected in the field blanks collected at S9, S5A, and S4. No pesticide analytes were detected in the two equipment blanks performed at S18C and S99. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. Matrix spike recoveries for 2,4-T, silvex, and Beta BHC, did not meet the specified requirements for the sediment samples collected at the following locations: S99, S2, S3 (including field duplicate) S4, S79, S78 (including field duplicate), S235, FECSR78, S65E, S191, S38B (including field duplicate), S140, S190, L3BRS, S8, S7, S6, S5A, ACME1DS (including field duplicate), and G94D. Matrix spike recoveries for 2,4-T and silvex did not meet the specified requirements for the sediment samples collected at the following locations: S331, US41-25, S12C, S31, S9, G123, S18C (including field duplicate), S178, S177, S332, S176, S355A, and S355B. The lab fortified blank and matrix spike recoveries for alpha BHC and gamma BHC did not meet the specified requirements for the surface water samples collected at the following locations: S99 (including equipment blank), GORDYRD, S80, S2 (including field blank), S3 (including field blank), S4, S79, CR33.5T, S78 (including field duplicate), S235, FECSR78, S65E, S191 (including field blank), S190, L3BRS, S8, S7 (including field blank), S38B (including field duplicate), NSIDWC06, and NSIDWC07. The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these

analyses and interpretation of the respective analytical results should consider this effect.

Glossary

- LD₅₀: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC₅₀: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC₅₀: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

- MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.
- PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.
- TEL: The threshold effects level represents the upper limit of the range of sediment contaminant concentrations dominated by no effect data entries, or the minimal effects range. Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms
- PEL: The probable effects level was calculated to define the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects or the lower limit of the probable effects range. Within the probable effects range, concentrations of sediment-associated contaminants are considered to represent significant and immediate hazards to aquatic organisms.

References

Adams, C.D. and E.M. Thurman. (1991). Formation and Transport of Deethylatrazine in the Soil and Vadose Zone. J. Environ. Qual. Vol. 20 pp. 540-547.

Callahan, M.A., M.W. Slimak, N.W. Gabel, I.P. May, C.F. Fowler, J.R. Freed, P. Jennings, R.L. Durfee, F.C. Witmore, B. Maestri, W.R. Mabey, B.R. Holt, and C. Gould. (1979). *Water-Related Environmental Fate of 129 Priority Pollutants, Volume I.* USEPA 440/4-79-029a.

Florida Department of Environmental Protection (1994a). *Florida Ground Water Guidance Concentrations*. Tallahassee, FL.

(1994b). Approach to the Assessment of Sediment Quality in Florida Coastal Waters, Volume I – Development and Evaluation of Sediment Quality Assessment Guidelines; prepared by MacDonald Environmental Sciences, Ltd. Ladysmith, British Columbia.

Goolsy, D.A., E.M. Thurman, M.L. Pomes, M.T. Meyer, and W.A. Battaglin. (1997). *Herbicides and Their Metabolites in Rainfall: Origin, Transport, and Deposition Patterns across the Midwestern and Northeastern United States, 1990-1991*. Environ. Sci. Technol. Vol. 31, No. 5, pp. 1325-1333.

Goss, D. and R. Wauchope. (Eds.) (1992). *The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure*. Soil Conservation Service. Fort Worth, TX.

Hartley, D. and H. Kidd. (Eds.) (1987). *The Agrochemicals Handbook*. Second Edition, The Royal Society of Chemistry. Nottingham, England.

Johnson, W.W. and M.T. Finley. (1980). *Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates*. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, DC.

Mayer, F.L. and M.R. Ellersieck. (1986) *Manual of Acute Toxicity: Interpretation and Database* for 410 Chemicals and 66 Species of Freshwater Animals. United States Fish and Wildlife Service, Publication No. 160

Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

Schneider, B.A. (Ed.) (1979). *Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data*. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W. (1992). *A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry*. Environ. Sci. Technol., Vol. 26, No. 12. pp. 2440-2447.

U.S. Environmental Protection Agency (1972).). *Effects of Pesticides in Water: A Report to the States*. U.S. Government Printing Office. Washington, D.C.

(1977). Silvacultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.
(1984). Chemical Fact Sheet for Simazine. March, 1984.
(1988). Chemical Fact Sheet for Hexazinone. September, 1988.
(1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, DC.
(1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B 96-002.

Verschueren, K. (1983). *Handbook of Environmental Data on Organic Chemicals*. Second Edition, Van Nostrand Reinhold Co. Inc. New York, NY.

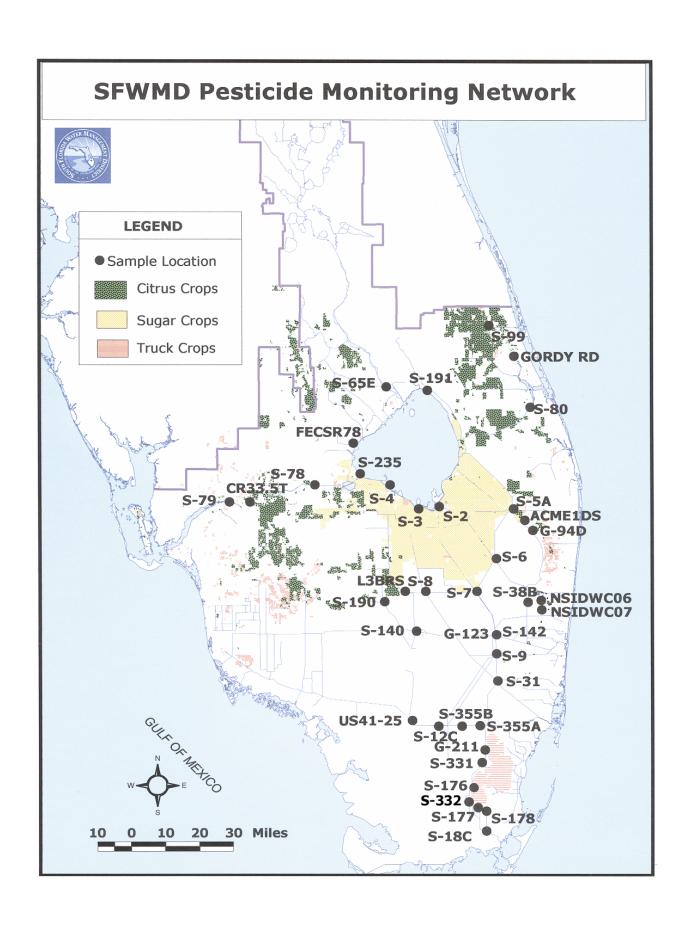


Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL) for pesticides determined in December 2001.

Pesticide or metabolite	Water: Range of MDL-PQL (ug/L)	Sediment: Range of MDL - PQL (ug/Kg)	Pesticide or metabolite	Water: Range of MDL-PQL (ug/L)	Sediment: Range of MDL - PQL (ug/Kg)
2,4-D	0.8 - 3.2	17 - 480	endosulfan sulfate	0.0045 - 0.0192	1 - 29.6
2,4,5-T	0.8 - 3.2	17 - 480	endrin	0.019 - 0.08	1.7 - 48
2,4,5-TP (silvex)	0.8 - 3.2	17 - 480	endrin aldehyde	0.0042 - 0.0176	0.83 - 23.6
alachlor	0.047 - 0.192	25 - 720	ethion	0.019 - 0.076	2.1 - 60
aldrin	0.0019 - 0.0088	0.41 - 11.6	ethoprop	0.019 - 0.076	4.1 - 116
ametryn	0.0094 - 0.0384	2.1 - 60	fenamiphos (nemacur)	0.028 - 0.116	17 - 480
atrazine	0.0094 - 0.38	2.1 - 60	fonofos (dyfonate)	0.019 - 0.076	4.1 - 116
atrazine desethyl	0.0094 - 0.0384	N/A	heptachlor	0.0023 - 0.0096	0.41 - 11.6
atrazine desisopropyl	0.0094 - 0.0384	N/A	heptachlor epoxide	0.0019 - 0.008	0.41 - 11.6
azinphos methyl (guthion)	0.019 - 0.076	2.1 - 60	hexazinone	0.019 - 0.076	8.3 - 236
α-BHC (alpha)	0.0021 - 0.0088	0.41 - 11.6	imidacloprid	0.2 - 0.4	N/A
β- BHC (beta)	0.0019 - 0.0132	0.41 - 11.6	linuron	0.2 - 0.4	8.3 - 120
δ-BHC (delta)	0.0021 - 0.0088	0.83 - 23.6	malathion	0.028 - 0.116	6.2 - 176
γ-BHC (gamma) (lindane)	0.0019 - 0.008	0.41 - 11.6	metalaxyl	0.047 - 0.192	N/A
bromacil	0.038 - 0.152	17 - 480	methamidophos	N/A	21 - 600
butylate	0.019 - 0.076	N/A	methoxychlor	0.0098 - 0.04	2.1 - 60
carbophenothion (trithion)	0.015 - 0.064	2.1 - 60	metolachlor	0.057 - 0.232	21 - 600
chlordane	0.0094 - 0.04	6.2 - 176	metribuzin	0.019 - 0.076	4.1 - 116
chlorothalonil	0.015 - 0.064	2.1 - 60	mevinphos	0.057 - 0.232	8.3 - 236
chlorpyrifos ethyl	0.019 - 0.076	2.1 - 60	mirex	0.011 - 0.048	1.7 - 48
chlorpyrifos methyl	0.0094 - 0.0384	4.1 - 116	monocrotophos (azodrin)	N/A	41 - 1160
cypermethrin	0.019 - 0.08	2.1 - 60	naled	0.075 - 0.308	34 - 960
DDD-P,P'	0.0045 - 0.0192	0.83 - 23.6	norflurazon	0.019 - 0.076	4.1 - 116
DDE-P,P'	0.0038 - 0.016	0.83 - 23.6	parathion ethyl	0.019 - 0.076	6.2 - 176
DDT-P,P'	0.0038 - 0.016	1.2 - 38.4	parathion methyl	0.019 - 0.076	6.2 - 176
demeton	0.11 - 0.48	41 - 1160	РСВ	0.019 - 0.08	0.08 - 520
diazinon	0.019 - 0.076	4.1 - 116	permethrin	0.015 - 0.064	2.5 - 72
dicofol (kelthane)	0.042 - 0.176	6.2 - 176	phorate	0.028 - 0.116	2.1 - 60
dieldrin	0.0019 - 0.008	0.41 - 11.6	prometryn	0.019 - 0.076	6.2 - 176
disulfoton	0.019 - 0.076	4.1 - 116	simazine	0.0094 - 0.0384	2.1 - 60
diuron	0.2 - 0.4	8.3 - 120	toxaphene	0.071 - 0.3	31 - 880
α-endosulfan (alpha)	0.0038 - 0.016	0.41 - 11.6	trifluralin	0.0075 - 0.032	1.1 - 48
β-endosulfan (beta)	0.0038 - 0.016	0.41 - 11.6	zinc phosphate	0.5 - 2	N/A

N/A - not analyzed

Table 2. Summary of pesticide residues (ug/L) in surface water samples collected by SFWMD in December 2001.

Date	Site	Flow	2,4-D	ametryn	atrazine	atrazine desethyl	atrazine desisopropyl	bromacil	diazinon	diuron	endosulfan sulfate	hexazinone	metolachlor	metribuzin	norflurazon	prometryn	simazine	Number of compounds detected at site
12/16/2001	G211	Υ	1	-	-	-	-	-	-	-	-	-	-	-	-	-		0
	S12C	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-		0
	S176	Υ	-	-	-	-		-	-	-	1	-	1	-	-	-		0
	S177	Υ	-	-	-	-	-	-	-	-	-	-	-	-	-	-		0
	S178	N	-	-	0.020 I	-	-	-	-	-	0.028	-	0.11 I	0.025 I	-	-		4
	S18C	N	-	-	-	-		-	-	-	-	-	-	-	-	-		0
	S331	Υ	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S332	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S335A	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	S355B	N	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
	US41-25	Υ	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0
12/17/2001	C25S99	N	-	-	-	-	0.027 I	-	-	-	-	-	-	-	1.3	-	0.38	3
	G123	N	-	-	0.010 I	-	-	-	-	-	-	-	-	-	-	-	- 0.046	1
	GORDYRD	Y	-	-	-	-	-	-	-	-	-	-	-	-	0.84	-	0.049	2
	S142	N	-	- 0.035 I	4.9	0.043	0.015 I	-	-	-	-	-	0.12 1	-	-	-	0.037 I	0
	S2 S3	N	-		_			-	-	-	-	- 0.024 l*	0.13 I	-	-	-		6
	S31	N	-	0.012 I [*]	0.15 * 0.013 I	0.036 I*	0.015 I *	-	-	-	-	0.024 1	-	-	-	-	0.022 I*	<u>6</u> 1
	S4	N N	-	0.70	3.7	0.069	0.020 I	-	-	-	-	0.024 I	-	-	-	-	0.032 I	6
	S80	N	-	0.70	3.1	0.069	0.020 1			-	-	0.024 1		-	0.63	-	0.032 1	2
	S9	Y		_			-	_	_	-	_	-	-	_	0.03		0.046	0
12/18/2001	CR33.5T	R	-	0.019 I	0.31	0.020 I	0.025 I	0.71		0.30 I	-				0.46	-	0.30	8
12/10/2001	FECSR78	Y	-	-	0.019 I	-	-	-	_	0.501				_	-		- 0.50	1
	L3BRS	N	_	0.018 I	0.022 1	_	_	_	_	_	_	_	_	_	_			2
	NSIDWC06	N	-	-	1.2	0.053	0.015 I	_	_	_	_	_	_	_	_		0.016 I	4
	NSIDWC07	N	-	0.027 I	2.0	0.14	0.022 I	_	_	0.22	_	_	_	_	_	_	-	5
	S190	N	_	-	-	-	-	_	_	-	_	_	_	_	0.041 I	-	-	1
	S191	N	-	-	-	-	_	-	-	-	_	_	_	_	-	-	-	0
	S235	N	-	0.022 I	0.051	-	_	0.046 I	-	-	-	0.021 I	_	_	0.035 I	-	-	5
	S38B	N	-	0.015 I	1.2	0.083	0.018 I	-	0.053 I	-	-	-	-	-	-	-	-	5
	S65E	N	-	-	0.096	0.018 I	_	-	-	-	-	-	_	-	-	-	-	2
	S 7	R	-	0.0097	-	-	-	-	-	-	-	-	-	-	-	-	-	1
	S78	N	-	0.052 *	0.75 *	0.044 *	0.017 I*	0.054 I*	-	-	-	0.024 *	-	-	0.30 *	-	0.024 1*	8
	S79	N	-	0.015 I	0.27	0.020 I	0.025 I	0.86	-	0.27 I	-	-	-	-	0.44	-	0.40	8
	S8	N	-	0.016 I	0.021 I	-	-	-	-	-	-	-	-	-	-	-	-	2
12/19/2001	ACME1DS	N	6.4	0.013 I	0.011 I	-	=	-	-	-	-	-	-	-	-	-	-	3
	G94D	N	-	-	0.00981	-	-	-	-	-	-	-	-	-	-	-	-	1
	S140	N	•	-	-	-	-	-	-	-	-	0.13	-	-	-	-	-	1
	S5A	N	-	0.041 *	0.56 *	0.019 I*	-	-	-	-	-	-	0.092 1*	-	-	-	-	4
	S6	N	-	0.15	0.40	-	-	-	-	-	-	-	-	-	-	0.021 I	0.020 I	4
Total number of o	compound detection	ons	1	15	21	11	10	4	1	3	1	5	3	1	8	1	11	

N – no Y – yes R – reverse; - denotes that the result is below the MDL; * - results are the average of duplicate samples; I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Summary of pesticide residues (ug/Kg) found in sediment samples collected by SFWMD in December 2001.

Date	Site	Flow	ametryn	bromacil	DDD-P,P'	DDE-P,P'	DDT-P,P'	diuron	norflurazon	PCB-1254	Number of compounds detected at site
12/17/2001	G123	N	-	200 I	-	-	-	49 I	-	-	2
l [S2	N	8.0 I	-	7.0 I	34	-	-	-	-	3
l [S3	N	-	-	6.9 I*	17 *	-	-	-	-	2
	S4	N	33	-	2.6 I	14	-	-	-	1	3
	S80	N	-	-	ı	-	-	-	15 I	1	1
12/18/2001	S79	N	-	-	ı	11 I	-	-	-	90 I	2
	S8	N	-	-	1.5 I	8.0	-	-	-	-	2
12/19/2001	S5A	Ν	-	-	13	40	150	-	-	310	4
	S6	N	-	-	-	9.3	-	-	-	-	1
Total num	ber of cor etections	mpound	2	1	5	7	1	1	1	2	

Table 4. Selected properties of pesticides found in December 2001 sampling event.

	i i			III December		J						
	Surface Water Standards 62-302	Ground Water Guidance Conc.	LD50 acute rats oral (mg/kg)	EPA carcinogenic	Water Solubility (mg/L)	Koc (mL/g)	Soil half-life (days)	scs	SCS rating (2)		Volatility from	Bioconcentratio
common name	(µg/L)	(µg/L)	(1)	potential	(2, 3)	(2, 3)	(2, 3)	LE	SA	SS	Water	Factor (BCF)
2,4-D (acid)	(100)	70**	375	D	890	20	10	М	S	М		13
ametryn	-	63	1,110	D	185	300	60	М	М	М		33
atrazine	-	3**	3,080	С	33	100	60	L	М	L	I	86
BHC-alpha	-	0.05	6,000	-	1.63	-	-	ı	-	-		469
bromacil	-	90	5,200	С	700	32	60	L	М	М	I	15
DDD, p,p'	-	0.1	3,400	-	0.055	239,900	-	ı	-	-		3,173
DDE, p,p'	-	0.1	880	-	0.065	243,220	-	ı	-	-	S	2,887
DDT, p,p'	0.001	0.1	113	-	0.00335	140,000	-	ı	-	-		15,377
diazinon	-	6.3	240 - 480	E	40	570	40	М	S	L		77
diuron	-	14	3,400	D	42	480	90	М	М	L		75
endosulfan-beta	-	0.35	70	-	0.28	-	-	-	-	-	S	1,267
endosulfan-sulfate	-	0.3	-	-	0.117	-	-	ı	-	-		2,073
hexazinone	-	231	1,690	D	33,000	54	90	L	М	М		2
metolachlor	-	1050	2,780	С	530	200	90	L	M	М		18
metribuzin	-	175	2,200	D	1,220	41	30	L	S	М		11
norflurazon	-	280	9,400	С	28	700	90	M	М	L		94
PCB's	0.014	0.5**	-	B2	-	-	-	-	-	-	-	-
prometryn	-	28	5,235	-	33	400	60	M	M	L		86
simazine	-	4**	>5,000	С	6.2	130	60	L	М	М		221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS)

Volatility from water: R = rapid, I = insignificant, S = significant

Bioconcentration Factor (BCF) calculated as BCF = 10^(2.791 - 0.564 log WS) (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards (4/95) for Class III waters except Class I in ()

Note: endosulfan usually considered the sum of alpha and beta isomers

- (1) Hartley, D. and H. Kidd. (Eds.) (1987)
- (2) Goss, D. and R. Wauchope. (Eds.) (1992)
- (3) Montgomery, J.H. (1993)
- (4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990)
- (5) U.S. Environmental Protection Agency (1996)

^{**} primary standard

Table 5. Toxicity of pesticides found in the December 2001 sampling event to freshwater aquatic invertebrates and fishes (ug/L).

	48 hr E	C50			96 hr LC	50			96 hr L0	`50			96 hr	C50	I	I	96 hr LC5	50			96 hr LC	50		
					Fathead Mir								Larger								Channe			
	Water				(#)				Blueg				Ва	ss			Rainbow Tro	,			Catfisl	h		
	Daphi	nia	acute	chronic	Pimephal	les	acute	chronic	Lepon	is	acute	chronic	Microp	terus	acute	chronic	Oncorhync	hus	acute	chronic	lctaluru	ıs	acute	chronic
common name	magr	na	toxicity (*)	toxicity (*)	promela	s	toxicity	toxicity	macroch	irus	toxicity	toxicity	salmo	ides	toxicity	toxicity	mykiss		toxicity	toxicity	punctat	us	toxicity	toxicity
2,4-D	25,000	(8)	8,333	1,250	133,000	(8)	44,333	6,650	180,000	(9)	60,000	9,000	-		-	-	100,000	(5)	33,333	5,000	-		-	-
	-		-	-	-		-	-	900 (48 hr	(7)	-	-	-		-	-	110,000	(8)	36,667	5,500	-		-	-
ametryn	28,000	(8)	9,333	1,400	-		-	-	4,100	(5)	1,367	205	-		-	-	8,800	(5)	2,933	440	-		_	-
atrazine	6900	(8)	2,300	345	15,000	(8)	5,000	750	16,000	(5)	5,333	800	-		-	-	8,800	(5)	2,933	440	7,600	(5)	2,533	380
BHC-alpha	-		-	-	-		-	-	-		-	-	-		-	-	-		-	-	-		-	-
bromacil	-		-	-	-		_	-	127,000	(8)	42,333	6,350	-		-	-	36,000	(8)	12,000	1,800	-		-	-
DDD, p,p'	3,200	(7)	1,067	160	4,400	(1)	1,467	220	42	(1)	14	2	42	(1)	14	2.1	70	(1)	23.3	3.5	1,500	(1)	500	75
DDE, p,p'	-		-	-	-		_	-	240	(1)	80	12	-		-	-	32	(1)	10.7	1.6	-		-	-
DDT, p,p'	-		-	-	19	(6)	6.3	0.95	8	(6)	2.7	0.4	2	(6)	0.7	0.10	7	(6)	2.3	0.35	16	(6)	5.3	0.8
diazinon	0.8	(1)	0.3	0.04	7,800	(8)	2,600	390	168	(1)	56	8.4	-		-	-	90	(1)	30	4.5	-		-	-
	0.9	(4)	0.3	0.045	-		-	-	165	(3)	55	8.3	-		-	-	1,650	(3)	550	83	-		-	-
	-		-	-	-		-	-	16,000	(5)	5,333	800	-		-	-	2,900	(5)	967	145	-		-	-
diuron	1,400	(8)	467	70	14,200	(8)	4,733	710	5,900	(5)	1,967	295	-		-	-	5,600	(5)	1,867	280	_		-	-
endosulfan	166	(8)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(8)	0.5	0.08
	-		-	-	-		_	-	-		-	-	-		-	-	1	(3)	0.33	0.050	-		-	-
	-		-	-	-		_	-	-		-	-	-		-	-	0.3	(6)	0.10	0.015	-		-	-
hexazinone	151,600	(8)	50,533	7,580	274,000	(5)	91,333	13,700	100,000	(8)	33,333	5,000	-		-	-	180,000	(8)	60,000	9,000	-		-	-
metolachlor	23,500	(8)	7,833	1,175	-		-	-	15,000	(5)	5,000	750	-		-	-	2,000	(5)	667	100	4,900	(6)	1,633	245
metribuzin	4,200	(8)	1,400	210	-		-	-	80,000	(5)	26,667	4,000	-		-	-	64,000	(5)	21,333	3,200	100,000	(8)	33,333	5,000
norflurazon	15,000	(8)	5,000	750	-		-	-	16,300	(8)	5,433	815	1		-	-	8,100	(8)	2,700	405	>200,000	(5)	>67,000	>10,000
prometryn	18,590	(8)	6,197	930	-		_	-	10,000	(5)	3,333	500	-		-	-	2,500	(5)	833	125	_		-	-
simazine	1,100	(8)	367	55	100,000	(8)	33,333	5,000	90,000	(5)	30,000	4,500	-		_	_	100,000	(8)	33,333	5,000	_		-	_

^(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aquatic community.

(#) Species is not indigenous. Information is given for comparison purposes only.

- (1) Johnson, W. W. and M.T. Finley (1980)
- (2) U.S. Environmental Protection Agency (1977)
- (3) Schneider, B.A. (Ed.) (1979)
- (4) U.S. Environmental Protection Agency (1972)
- (5) Hartley, D. and H. Kidd. (Eds.) (1987)
- (6) Montgomery, J.H. (1993)
- (7) Verschueren, K. (1983)
- (8) U.S. Environmental Protection Agency (1991)
- (9) Mayer, F.L., and M.R. Ellersieck. (1986)

Table 6. Atrazine Desethyl/Atrazine ratio (DAR) data for December 2001.

Site	Flow	atrazine ug/l	Moles/L	atrazine desethyl ug/l	Moles/L	DAR
S2	N	4.9	2.27183E-08	0.043	2.29173E-10	0.0
S3	N	0.145	6.72276E-10	0.0355 I *	1.89201E-10	0.3
S4	N	3.7	1.71546E-08	0.069	3.67742E-10	0.0
CR33.5T	Y	0.31	1.43728E-09	0.02 I	1.06592E-10	0.1
NSIDWC06	N	1.2	5.56367E-09	0.053	2.82469E-10	0.1
NSIDWC07	N	2	9.27278E-09	0.14	7.46143E-10	0.1
S38B	N	1.2	5.56367E-09	0.083	4.42356E-10	0.1
S65E	N	0.096	4.45093E-10	0.018 I	9.59327E-11	0.2
S78	N	0.745	3.45411E-09	0.0435 *	2.31837E-10	0.1
S79	N	0.27	1.25182E-09	0.02 I	1.06592E-10	0.1
S5A	N	0.555	2.5732E-09	0.0185 I *	9.85975E-11	0.0
	-	•	DAR	All sites	Flow only sites	No flow sites
			average	0.1	0.1	0.1
			median	0.1	0.1	0.1
			minimum	0.0	0.1	0.0
			maximum	0.3	0.1	0.3

Figure 2. Endosulfan Concentration in Surface Water at S178

